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Discussion Section: (Janette, Peter, Richard, Stephen)

1. Three odd looking bodies are found in the Berkeley Hills. There is some thought that one is human and the other two are alien. You are a forensic biologist that SETI has called in to make the ID. But being a secretive organization they only provide you hemoglobin samples from the three bodies. You perform experiments on the three different proteins to determine if they are of human origin. Human hemoglobin is about 6.68×10^4 g/mol, is a cooperative binder of oxygen molecules, and is awfully good at delivering oxygen to tissue.

a) The first thing you do is measure the osmotic pressure of the three proteins at 25 C.

Concentration (mg/mL)	Osmotic Pressure (mm Hg) (1 atm = 760 mm Hg)		
	Protein1	Protein2	Protein3
9.0	2.51	2.45	9.8

What are the molecular weights of the proteins?

+3

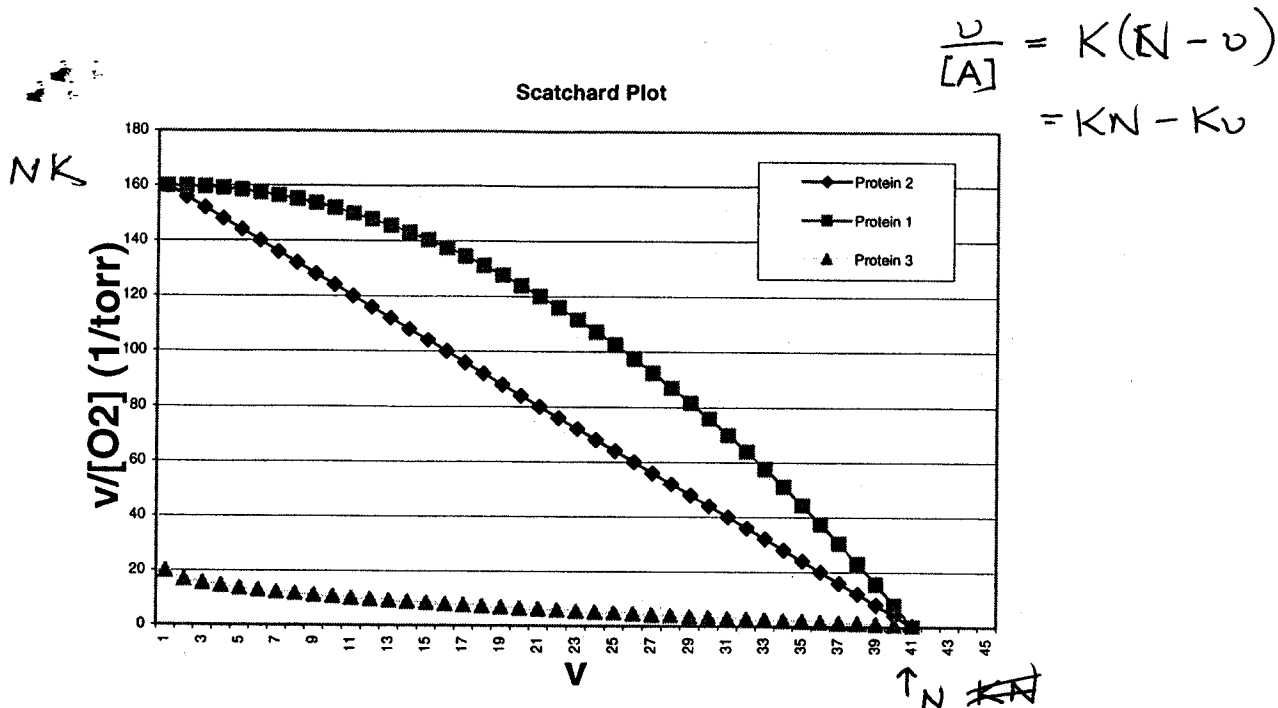
$$\left\{ \begin{array}{l} \pi = CRT. \\ C_1 = \frac{\pi}{RT} = \frac{2.51/760}{0.08206 \cdot 298} = 1.35 \times 10^{-4} \\ C_2 = \frac{\pi}{RT} = \frac{2.45/760}{0.08206 \cdot 298} = 1.32 \times 10^{-4} \\ C_3 = \frac{\pi}{RT} = \frac{9.8/760}{0.08206 \cdot 298} = 5.27 \times 10^{-4} \end{array} \right.$$

+2

$$\left\{ \begin{array}{l} mw_1 = \cancel{668} \ 6.67 \times 10^4 \ \frac{g}{mol} \\ mw_2 = 6.82 \times 10^4 \ \frac{g}{mol} \\ mw_3 = 1.71 \times 10^4 \ \frac{g}{mol} \end{array} \right.$$

$$\frac{v}{[A]} = K(1-v)$$

b) Well, obviously without even solving part (a) we know that protein 1 and protein 2 have similar molecular weights. Let's see if these proteins bind oxygen like expected. You perform an equilibrium dialysis experiment and measure the concentration of free and bound oxygen to make a Scatchard plot. Here are the results:



For protein 2, Calculate the binding constant for oxygen and how many molecules of oxygen are bound per macromolecule?

$$K = \frac{\text{y-intercept}}{\text{x-intercept}} = \frac{160}{41} = \underline{3.9}$$

$$N = 41$$

+2

Why aren't the plots for proteins 1 and 3 linear? Why is the plot for protein 1 curved upward and that for protein 3 curved downward?

Protein 1 is co-operative binding
Protein 3 is anti co-operative binding.

Non-independent.

+3

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$$\frac{f}{1-f} = K[A]^n$$

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$$1 = 40 K_2 \quad K_2 = 40$$

10pt c) Assume the binding concentration of O₂ is 40 Torr at half-maximal binding for proteins 1 & 2 and 10 Torr for Protein 3. Given that proteins 1, 2, and 3 have Hill coefficients of 3, 1, and 0.6 respectively, rank the effectiveness of oxygen delivery to tissue for all three proteins. Effectiveness is gauged as the ability of a protein to bind the most O₂ at 100 Torr (lung) and the least at 20 Torr (tissue)--for a given amount of protein. Prove your results by calculation.

$$1 = K_1 [40]^3 \quad K_1 = 1.56 \times 10^{-5}$$

$$1 = K_2 [40]^1 \quad K_2 = 2.5 \times 10^{-2}$$

$$1 = K_3 [10]^{0.6} \quad K_3 = 2.5 \times 10^{-1}$$

} +5

100 Torr:

$$\frac{f_1}{1-f_1} = 1.56 \times 10^{-5} [100]^3 = 15.6$$

$$\frac{f_2}{1-f_2} = 2.5 \times 10^{-2} [100] = 2.5$$

$$\frac{f_3}{1-f_3} = 2.5 \times 10^{-1} [100]^{0.6} = 4.0$$

20 Torr:

$$\frac{f_1}{1-f_1} = 0.125$$

$$\frac{f_2}{1-f_2} = 0.5$$

$$\frac{f_3}{1-f_3} = 1.51$$

} +5

If simply use "n" as a measure:

+3

5pt d) So based on your answers to the last questions, which one is the human hemoglobin and why?

+1 Protein 1. ① mw is similar

+2 ② Cooperative

+2 ③ $\frac{f}{1-f}$ is great in 100 torr and least in 20 torr

20

2. A newly discovered bacterium trying to survive somewhat north of the South Pole has to contend with a very sensitive freeze thaw cycle. It turns out that its environment wobbles a degree or two around freezing during the day. A biologist studying this system notices that the cell expresses a protein that becomes more active at cold temperatures. Noticing the cell doesn't freeze and seems to uptake protein synthetic precursors, she hypothesizes that the protein stimulates synthesis of many other small proteins (that can't leave the cell) that act to cause a freezing point depression.

- x5
5 a) Assuming the cell behaves like water and is a femtoliter (10^{-15} L) in volume, approximately how many particles would the cell have to synthesize to prevent freezing at two degrees below the freezing point of pure water.

$$\Delta T_f = K_f m_b$$

$$2^\circ\text{C} = 1.86 \frac{\text{K} \cdot \text{kg solvent}}{\text{moles solute}} m_b$$

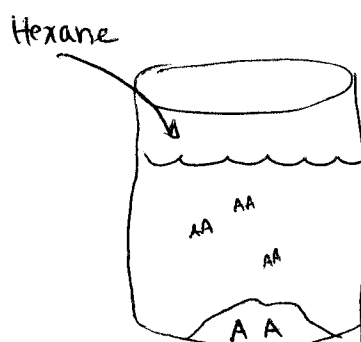
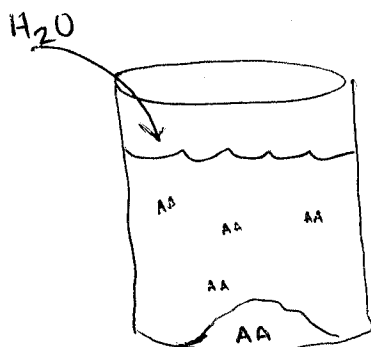
$$m_b = \frac{2}{1.86} \frac{\text{moles solute}}{\text{kg solvent}}$$

no of particles needed in femtoliter \rightarrow

$$N_b = \frac{2}{1.86} \frac{\text{moles solute}}{\text{kg solvent}} \left(\frac{1 \text{ kg H}_2\text{O}}{1 \text{ L H}_2\text{O}} \right) \left(10^{-15} \text{ L H}_2\text{O} \right) \left(\frac{6.022 \times 10^{23} \text{ particles}}{1 \text{ mol solute}} \right)$$

$$= 6.47 \times 10^8 \text{ particles}$$

c) It turns out this expressed macromolecule has some interesting properties. You find that your protein contains a novel amino acid. You want to get a thermodynamic measure of its hydrophobicity. You place an excess amount of solid amino acid in equilibrium with water and, in a separate jar, you place an excess amount of solid amino acid in equilibrium with hexane. The solubility of the amino acid in the two solvents is measured spectroscopically and found to be 1 millimolar and 10 nanomolar (10^{-8} M) respectively. At 37°C , what is the difference in standard chemical potential for transfer of the amino acid from water to hexane using 1 molar solute as the standard state?



AA \equiv amino acid.

$T = 37^\circ\text{C}$

$$[\text{AA}]_{\text{H}_2\text{O}} = 1 \text{ mM} \\ = 1 \times 10^{-3} \text{ M}$$

$$[\text{AA}]_{\text{Hexane}} = 10 \text{ nM} \\ = 10^{-8} \text{ M}$$

$$\mu_{\text{AA}}(\text{solid}) = \mu_{\text{AA}}(\text{H}_2\text{O})$$

$$\mu_{\text{AA}}(\text{solid}) = \mu_{\text{AA}}(\text{Hexane})$$

Therefore,

$$\mu_{\text{AA}}(\text{H}_2\text{O}) = \mu_{\text{AA}}(\text{Hexane}).$$

$$\mu_{\text{AA}}^\circ(1 \text{ M in H}_2\text{O}) + RT \ln a_{\text{AA}}(\text{H}_2\text{O}) = \mu_{\text{AA}}^\circ(1 \text{ M in Hexane}) + RT \ln a_{\text{AA}}(\text{Hexane})$$

Taking difference in μ° ,

$$\mu_{\text{AA}}^\circ(1 \text{ M in Hexane}) - \mu_{\text{AA}}^\circ(1 \text{ M in H}_2\text{O}) = RT \ln a_{\text{AA}}(\text{H}_2\text{O}) - RT \ln a_{\text{AA}}(\text{Hexane})$$

$$\Delta \mu^\circ = RT \ln \frac{a_{\text{AA}}(\text{H}_2\text{O})}{a_{\text{AA}}(\text{Hexane})}$$

Assuming $a_{\text{AA}} \approx [\text{AA}]$

$$\Delta \mu^\circ = RT \ln \frac{[\text{AA}]_{\text{H}_2\text{O}}}{[\text{AA}]_{\text{Hexane}}} \\ = (8.31 \frac{\text{J}}{\text{K}})(273+37 \text{ K}) \ln \left(\frac{10^{-3}}{10^{-8}} \right) \\ = 2.97 \times 10^4 \text{ J} \quad \text{+1 calc. or T}$$

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3. An element is defined by the number of protons in its nucleus (and electrons) and it is this number which determines its gross chemical behavior. Typically, there are many isotopes of each element in the Periodic Table which differ only by the number of neutrons in the nucleus (e.g. there are 15 known isotopes of Carbon-element 6- of which 3 occur in nature). Because their chemical properties are virtually identical, methods have been developed to separate isotopes based upon the small differences in certain properties.

Uranium, element 92, has two isotopes which occur in nature:

Isotope	Mass (g/mol)	abundance (%)
^{235}U	235	00.7204
^{238}U	238	99.2796

^{235}U is important in certain industries and various techniques have been developed to enrich its concentration. In the US, one of the principal means of enrichment is by gaseous diffusion. In this process, uranium hexafluoride (UF_6) is heated to a vapor and fed at high pressure and diffuses through a porous barrier to a low pressure side. Assume each fluorine atom has a mass of 19g/mol.

a) Calculate the mean square speeds of each isotope of UF_6 assuming $T = 70^\circ\text{C}$ (boiling point).

$$W(^{235}\text{UF}_6) = 235 + 6 \cdot 19 = 349 \frac{\text{g}}{\text{mol}}$$

$$\langle u^2 \rangle = \frac{3KT}{m} = \frac{3RT}{W}$$

$$\langle u^2 \rangle_{^{238}\text{UF}_6} = 24,300 \left(\frac{\text{m}}{\text{s}} \right)^2$$

$$W(^{238}\text{UF}_6) = 352 \frac{\text{g}}{\text{mol}}$$

$$\langle u^2 \rangle_{^{235}\text{UF}_6} = \frac{3 \cdot 8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot 343 \text{K}}{0.349 \text{ kg/mol}} = 24,500 \left(\frac{\text{m}}{\text{s}} \right)^2$$

Avogadro's # $\rightarrow AK = R \quad AM = W$

b) We define the *maximum separation factor* (α^*) as the ratio of the velocities of the two molecules. Calculate α^* (using the molecular masses) for the separation of the two isotopes of UF_6 by effusion.

$$\frac{\langle u \rangle_{^{235}\text{UF}_6}}{\langle u \rangle_{^{238}\text{UF}_6}} = \sqrt{\frac{W(^{238}\text{UF}_6)}{W(^{235}\text{UF}_6)}} = \sqrt{\frac{352}{349}} = 1.004$$

c) Another method of enriching ^{235}U is by Gas Centrifuge Separation, where α^* is determined by the *difference* in the masses of the two molecules. Is this method better or worse than a method that depends on the ratio of the masses, and why?

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d) Given the atomic diameter of Uranium is 2 angstroms what is its mean free path in gaseous form at 1 atmosphere?

$$\sigma = 2 \times 10^{-10} \text{ m}$$

$$\lambda = \frac{\langle u \rangle}{z} \quad z = \sqrt{2} \pi \frac{N}{V} \sigma^2 \langle u \rangle \quad PV = nRT = \frac{N}{A} RT$$

$$\lambda = \frac{1}{\sqrt{2}} \frac{1}{\pi} \frac{1}{\sigma^2} \frac{V}{N} \quad \hookrightarrow \frac{N}{V} = \frac{PA}{RT}$$

$$\lambda = \frac{1}{\sqrt{2}} \frac{1}{\pi} \frac{1}{\sigma^2} \cdot \frac{RT}{PA}$$

$$\lambda = \frac{1}{\sqrt{2}} \frac{1}{\pi} \frac{1}{(2 \times 10^{-10} \text{ m})^2} \cdot \frac{8.31 \frac{\text{J}}{\text{K} \cdot \text{mol}} \cdot 343 \text{ K}}{1.01 \times 10^5 \frac{\text{N}}{\text{m}^2} \cdot 6.02 \times 10^{23} \frac{1}{\text{mol}}}$$

$$= \boxed{2.64 \times 10^{-7} \text{ m}}$$